

## LITHOGRAPHIC DRY DEVELOPMENT USING OPTICAL ABSORPTION

### CROSS REFERENCE TO RELATED APPLICATIONS

**[0001]** This application claims priority to Provisional U.S. Patent Application No. 61/320,929 filed Mar. 4, 2010, entitled Lithographic Dry Development Using Optical Absorption, a copy of said earlier application incorporated herein as if fully set forth in its entirety.

### STATEMENT OF GOVERNMENTAL SUPPORT

**[0002]** The invention described and claimed herein was made in part utilizing funds supplied by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 between the U.S. Department of Energy and the Regents of the University of California for the management and operation of the Lawrence Berkeley National Laboratory. The government has certain rights in this invention.

### BACKGROUND OF THE INVENTION

**[0003]** 1. Field of the Invention

**[0004]** This invention relates generally to lithographic development of photo resist materials and, more specifically a new method and class of compounds for dry development and processing of photoresist using laser based optical absorption and ablation.

**[0005]** 2. Description of the Related Art

**[0006]** Lithography has become an important tool in semiconductor manufacturing, especially in the removal such as by etching or the deposition of certain materials onto a supporting wafer, from which individual chips will eventually be formed. Generally, a resist material is first placed on a wafer as a blanket coating across the wafer surface. This can be done in any one of several ways, one of the most widely used methods being the spin on of resist coatings, usually a polymer, dissolved in a solvent so that it is in liquid form. Thereafter, with the wafer coated with resist, it is subject to a lithographic step where the resist is subject to exposure to a light/energy source, such as EUV or visible light. In the usual case the light/energy source is projected through a lithographic mask to create an exposure pattern on the resist, the wafer subject to numerous exposure steps in order to fully expose the wafer surface. The resist itself undergoes a chemical change in the areas where exposure has occurred, to change the solubility of the material. The exposure is repeated until the entire surface of the wafer has been exposed. Commonly a stepper will be employed, the tool providing for the precision movement of the wafer from one position to another so that with each exposure an adjacent but non overlapping area of the wafer is exposed.

**[0007]** In the lithography process both positive and negative resists are used. For positive resists, the resist is exposed with light projected through a mask, the mask containing an exact copy of the pattern to remain on the wafer. Thus, only in the exposed areas, where the underlying material is to be removed does the exposure change the chemical structure of the resist such that it becomes more soluble in the developer. The exposed resist is then washed away using the developer solution, exposing the underlying material. The wafer is then subject to further processing, be it etch or deposition.

**[0008]** For a negative resist, the materials behave in the opposite manner. Exposure to light causes the negative resist

to further polymerize, thus making it less soluble in the developer. Therefore the negative resist will remain on the surface of the wafer wherever it has been exposed, and the development solution will remove the resist only in the unexposed areas. Thus, masks used with negative resists contain the inverse (i.e. the photographic negative) of the pattern to be transferred.

**[0009]** One particularly useful method for patterning very small, nano-scale features, employs an electron beam writer instead of stepper to create the desired patterns. Here, the resist is put on in the traditional manner. Instead, however, of using a mask to transfer a pattern, an electron beam is used to "write" the pattern onto the substrate by moving the e-beam across the resist in the areas to be patterned. This maskless approach has found particular utility in the making of the lithographic masks themselves, which masks are then used in EUV/visible light lithography processes. In yet another e-beam approach, a broad e-beam is used, much like with EUV, where the e-beam is projected through a mask to expose the resist in those areas struck by the beam.

**[0010]** No matter the approach, the resist is chemically changed as the result of the exposure to the energy source, be it UV light or e-beam, the resulting exposure causing a change in the solubility of the resist. In a next step, the resist is washed away using a solvent, the resist remaining on the substrate where exposed (in the case of a negative resist) or washed away where exposed (in the case of a positive resist). Thereafter, the remaining resist can be hardened, for instance by heating, before a final washing step is performed, all of this preparatory to subsequent etching or deposition. These processes are well known and are not further described herein.

**[0011]** As features have gotten smaller and smaller and aspect ratios higher and higher, problems have arisen relating to pattern collapse as a result of the steps used to remove the resist. It has been reported, in fact, in the case of very small features having high aspect ratios, that the mere capillary (i.e. surface tension) forces of the liquid solvent within the trenches of the resist generated during the drying process is sufficient to cause pattern wall collapse. As feature sizes continue to shrink, resist collapse has been found to occur at smaller and smaller aspect ratios and for features 50 nm or less, it can happen at aspect ratios less than 2. For more on this phenomenon, see K. Yoshimoto, P. Stoykovich, H. B. Cao, J. J. de Pablo, P. F. Nealey, and W. J. Dragan, *J. Appl. Phys.* 96, 1857 (2004), or the review discussing challenges for EUV lithography by B. Wu and A. Kumar, *J. Vac. Sci. Technol. B*, 25, 1743 (2007).

**[0012]** To address this problem, several solutions have been proposed. One such suggested approach is directed to reducing the capillary pressures acting on the exposed resist, such as by drying using lower surface tension solvents, supercritical drying, or freeze drying, as well as using surfactants to lower capillary forces. Still other approaches have been directed to improving the photoresist's mechanical properties, such as by increasing the Young's modulus of the photo resist polymer.

**[0013]** Still other approaches to overcoming this phenomenon have included dry development such as reported by Vertommen, J. K., A. Klippert, W. Goethals, A.-M. Van Roey, F. in Integrated Silylation and Dry Development of Resist for Sub 0.15 m, *Top Journal of Photopolymer Science and Technology*, 1998, Vol. 11; Number 4, pages 597-612. In this chemical approach, silicon containing gases are introduced to the wafer where they react with the photoresist film (a silyla-